Soil Phosphorus Compositional Characteristics as a Function of Land-Use Practice in the Upper Eau Galle River Watershed, Wisconsin

by William F. James, Harry L. Eakin, Carlos E. Ruiz, and John W. Barko

PURPOSE: The purpose of this research was to quantify biologically labile and refractory phosphorus species in source soils of an agricultural watershed that drains into a eutrophic Corps of Engineers reservoir.

BACKGROUND: Eutrophication of receiving waters is strongly linked to the erosion and transport of particulate and soluble nutrients derived from the watershed landscape. In dairy and agricultural settings, amendment of soils with fertilizers and manure is usually based on crop nitrogen (N) requirements rather than phosphorus (P) to obtain optimal yield. In particular, various manures also have a high P content; usually well in excess of crop uptake requirements with N:P ratios near 1 (Powers and Van Horn 1998). Thus, applications based on crop N requirements usually result in the buildup of soil P levels to excessive concentrations that can be transported to receiving waters during storms (Sharpley et al. 1994).

For watershed modeling applications that assess P runoff from agricultural landscapes, and impacts on lakes and reservoirs, more information is needed on forms of P in soils that may become biologically labile (i.e., subject to direct uptake or recycling pathways) or refractory (i.e., not readily available to the biota and subject to burial) as runoff moves through the landscape and into receiving waters. Soil test phosphorus assays are accurate in assessing P availability for crop uptake but may not be applicable input for modeling the impacts of runoff and P transformations on aquatic biological uptake or recycling in receiving waters (Sharpley et al. 1994). For instance, metal hydroxides associated with soils play an important role in P equilibrium reactions between particulate and aqueous phases as runoff moves through tributaries and into lakes or reservoirs (McDowell et al. 2001; McDowell and Sharpley 2003). Accretion of this watershed-derived material and associated P in receiving waters can lead to later P recycling via eH and pH reactions (James et al. 1995, 1996). Accreted sediment P can also be recycled by aquatic plants through root uptake and senescence and become a source of algal productivity (James et al. 2002). These recycling pathways, referred to as internal P loads, can sustain algal productivity for many years, even when external P loads are nominal or reduced by best management practices (BMP’s).

P fractionation techniques have been developed to differentiate biologically labile and refractory P species in total suspended solids and aquatic sediments of receiving waters (Psenner and Puckso 1988; Southern Extension/Research Activity-Information Exchange Group (SERA-IEG) 2000; Table 1). Similar P differentiation for soils in the watershed may provide greater insight

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **SEP 2004**	2. REPORT TYPE	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Soil Phosphorus Compositional Characteristics as a Function of Land-Use Practice in the Upper Eau Galle River Watershed, Wisconsin**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Army Engineer Research and Development Center,Environmental Laboratory,3909 Halls Ferry Road,Vicksburg,MS,39180-6199**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
The original document contains color images.

14. ABSTRACT
see report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**12**	

Table 1
Operationally Defined Phosphorus Fractions[1]

Variable	Extractant	Biological Availability and Susceptibility to Recycling Pathways
Loosely bound P	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Iron-bound P	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Aluminum-bound P	0.1 N sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial.
Calcium-bound P	0.5 N hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial.
Labile organic-polyphosphate P	Persulfate digestion of the NaOH extraction	Biologically labile; Polyphosphates are available for biological uptake. Also recycled via bacterial mineralization and surplus storage in cells
Refractory organic P	Persulfate digestion of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial.

[1] Labile = Subject to recycling pathways or direct availability to the biota.
Refractory = Low biological availability and subject to burial.

into their susceptibility to recycling pathways and bioavailability in receiving waters and improve mechanistic modeling algorithms for computing P transformations. In addition, distinction of labile and refractory P species in soils may provide unique source signatures that can be used to evaluate the relative contribution of different land-use practices and biological availability to P loads entering receiving waters. The objectives of this study were to evaluate labile and refractory P components of soils as a function of land use in a Wisconsin watershed dominated by agriculture and dairy production.

METHODS: The Upper Eau Galle River basin drains a 123.3-km^2 watershed above the Eau Galle Reservoir, a Corps of Engineers impoundment that provides flood protection and recreation (Figure 1). Agricultural land uses are dominated by annual and perennial crop production (i.e., corn, oats, alfalfa, grass hay, soy beans), pasture, and livestock dairy production. Other land uses include CRP (Conservation Reserve Program) and wooded areas. The watershed is located within the glaciated region of Wisconsin and the dominant soil associations are the Vlasaty-Skyberg, located in the eastern portion of the watershed, and Saltre-Pillot Antigo, located in western portions (Ashby 1985).

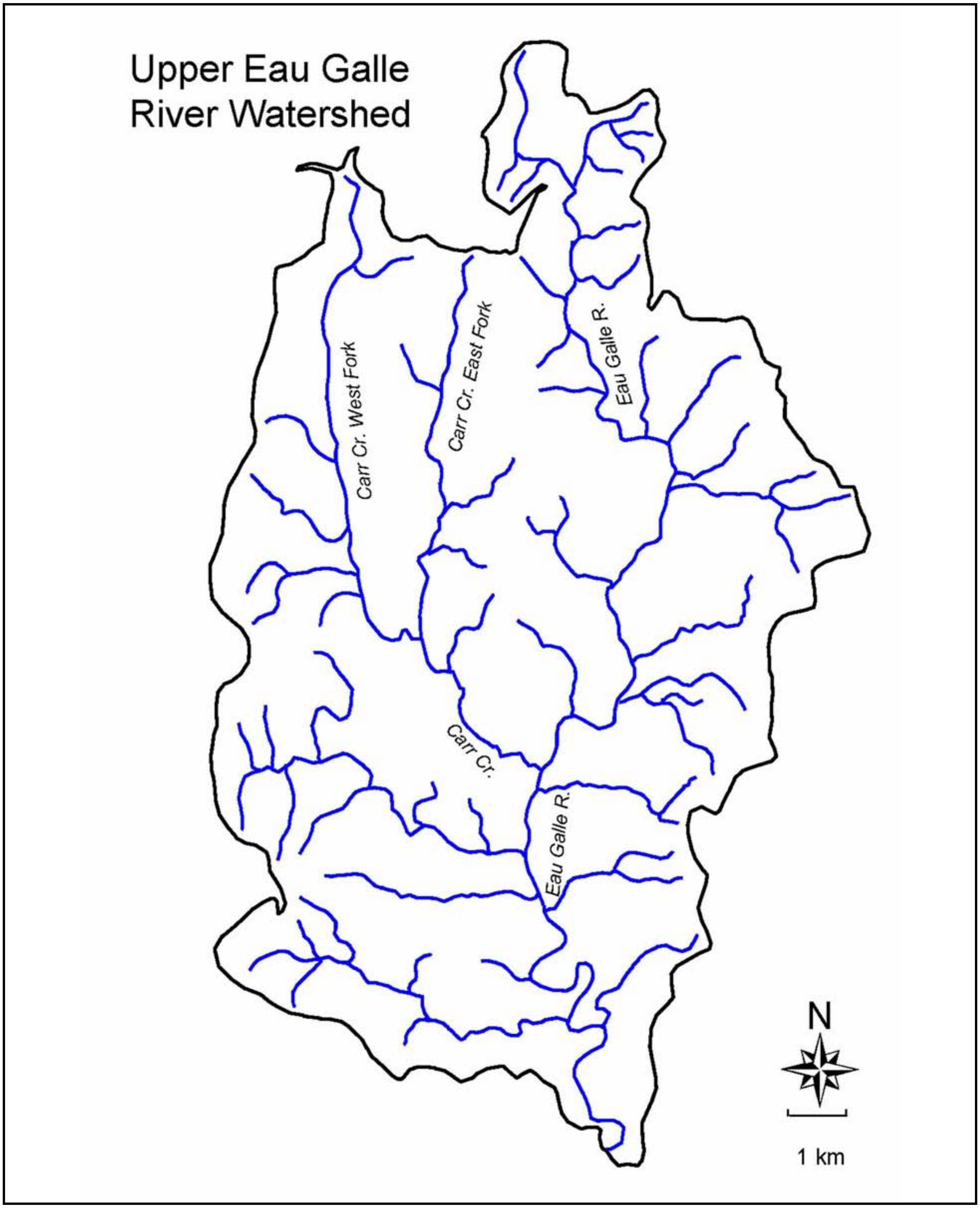

Figure 1. Upper Eau Galle River watershed

During the winter of 2001-02, the Upper Eau Galle River Watershed was examined for different land-use practices (by vehicle) and six land-use categories were chosen for soil sampling purposes (Table 2). Letters were sent to ~ 250 landowners in the watershed requesting permission to sample soils on their land; the response was ~30 percent. Volunteers for the soil survey were personally interviewed about the different land-use practices on their property and 81 sites representing different land uses were chosen for soil sampling.

Table 2
Land-Use Practices and Numbers of Soil Samples (N) Collected in Each Category[1]

Land Use	N
Alfalfa fields	13
Barnyard areas	9
Cornfields	21
CRP	13
Forage pastures	9
Woodlots	16

[1] CRP = Conservation Reserve Program

Soil sampling was conducted in late June through early July 2002. The goal of the soil sampling was to attempt to characterize soil properties as a function of land-use practice on a watershed-wide scale instead of a field plot scale. Thus, no attempt was made to examine field-scale variability in soil characteristics. Land-use soil sampling was also stratified as a function of location in the watershed. Thus, soil samples from cornfields were taken in several different locations throughout the watershed. Soils were collected at least 15 m inside of each land-use area to minimize edge effects. At each site, three replicate samples of the upper 5 cm of soil were collected using a 5-cm-diam tube corer and composited into one sample. In the laboratory, soil samples were sieved through a 2-mm mesh screen, air-dried, and stored in a desiccator until analysis.

The soil organic content was estimated as loss on ignition (LOI) by combusting soil at 500 °C for 24 hr. The percentage of sand (> 63 μ), silt (between 2 μ and 63 μ), and clay (< 2 μ) was determined using a combination of sieving and pipette techniques (Plumb 1981). Total P was analyzed colorimetrically following block digestion with sulfuric acid, potassium sulfate, and red mercuric oxide (Plumb 1981). Mehlich-3 crop-available P was determined according to Mehlich (1984). Water-soluble P was extracted for 1 hr using 10 mL deionized water to 1 gram of dried soil, centrifuged, and filtered through a 0.45-μm membrane filter for analysis of soluble reactive P (SERA-IEG 2000). Inorganic P in the soils was sequentially fractionated according to Hieltjes and Lijklema (1980) and Nürnberg (1988) to determine ammonium-chloride-extractable P (loosely bound P), bicarbonate-dithionite-extractable P (i.e., iron-bound P), sodium hydroxide-extractable P (i.e., aluminum-bound P), and hydrochloric acid-extractable P (i.e., calcium-bound P). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable PP (Psenner and Puckso 1988). Labile particulate organic-polyphosphate P was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable P. Remaining P after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid for determination of refractory organic P. Each extraction was filtered through a 0.45-μm filter, adjusted to pH 7, and analyzed for SRP using the ascorbic acid method (American Public Health Association (APHA) 1998).

RESULTS AND DISCUSSION: Mean P concentrations patterns varied as a function of land-use category (Figure 2). Barnyard soils exhibited significantly greater mean concentrations of total P than other land-use practices. However, there were no significant differences in mean total P between the other agriculturally managed (i.e., forage pastures, alfalfa fields, and cornfields) and unmanaged (i.e., CRP and woodlots) land uses. Mean Mehlich-3 P, water-soluble P, and loosely bound P exhibited a trend of barnyard soils >> agriculturally managed soils > unmanaged soils. A similar, but statistically weaker, trend was observed for mean iron-bound, aluminum-bound P, and refractory organic P over the different land-use categories. Mean calcium-bound P and labile organic P exhibited no clear trends in concentration as a function of soil management. Overall, it appeared that mean Mehlich-3 P concentrations were well above P threshold concentrations required for optimal crop yield (0.04-0.05 mg g-1; Fixen 1998; Sharpley et al. 1994) for all land uses except woodlots.

Like P concentrations, the mean LOI content was significantly greater for barnyard soils versus other land uses (Figure 3). Forage pasture, CRP, and woodlot soils had a significantly greater mean LOI content than alfalfa and cornfields. The particle composition of soils was similar among all land uses except barnyard soils. These latter soils were composed of 60 percent sand, 32 percent silt, and 8 percent clay. Soils in other land uses had a higher silt content (range of means = 49 to 56 percent). Clay content was minor for all land uses examined (i.e., < 8 percent).

When considered as a percentage composition of the total soil P concentration, there were some significantly different patterns for different land uses (Figure 4). For instance, a trend of greater mean percent composition of loosely bound P was observed for managed soils (barnyards, forage pasture, alfalfa fields, and cornfields) versus unmanaged soils collected in woodlot and CRP land uses. In contrast, the P composition of woodlots and CRP was dominated by labile organic P versus soils in managed land-use areas.

Correlation matrices between variables suggested that P fractions might be useful in distinguishing the origins of soils from different land uses in the watershed (Table 3). For barnyard soils, strong correlations were found between total P, Mehlich-3 P, water-soluble P, and loosely bound P versus other variables. Forage pasture soils exhibited a similar, but not exact, correlation matrix pattern as that of barnyard soils, which may be due to livestock manure inputs on forage fields. Like barnyard soils, soils from alfalfa and cornfields also exhibited strong correlations between total P, Mehlich-3 P, water-soluble P, and loosely bound P. In addition, these annual and perennial crop production soils also exhibited strong correlations with iron-bound and loosely bound P. Soils from CRP and woodlot land uses had very few significant or meaningful correlations between different soil P variables. Total P was significantly correlated with aluminum-bound P for soils in both land-use categories and it was correlated with refractory organic P in woodlot land-use settings. Unlike the agriculturally managed land uses, significant correlations did not exist between many of the more biologically labile P forms and total P for CRP and woodlot soils.

Correlation patterns suggested that soils in agriculturally managed land-use areas exhibited strong relationships primarily between total P and forms of P that are typically associated with

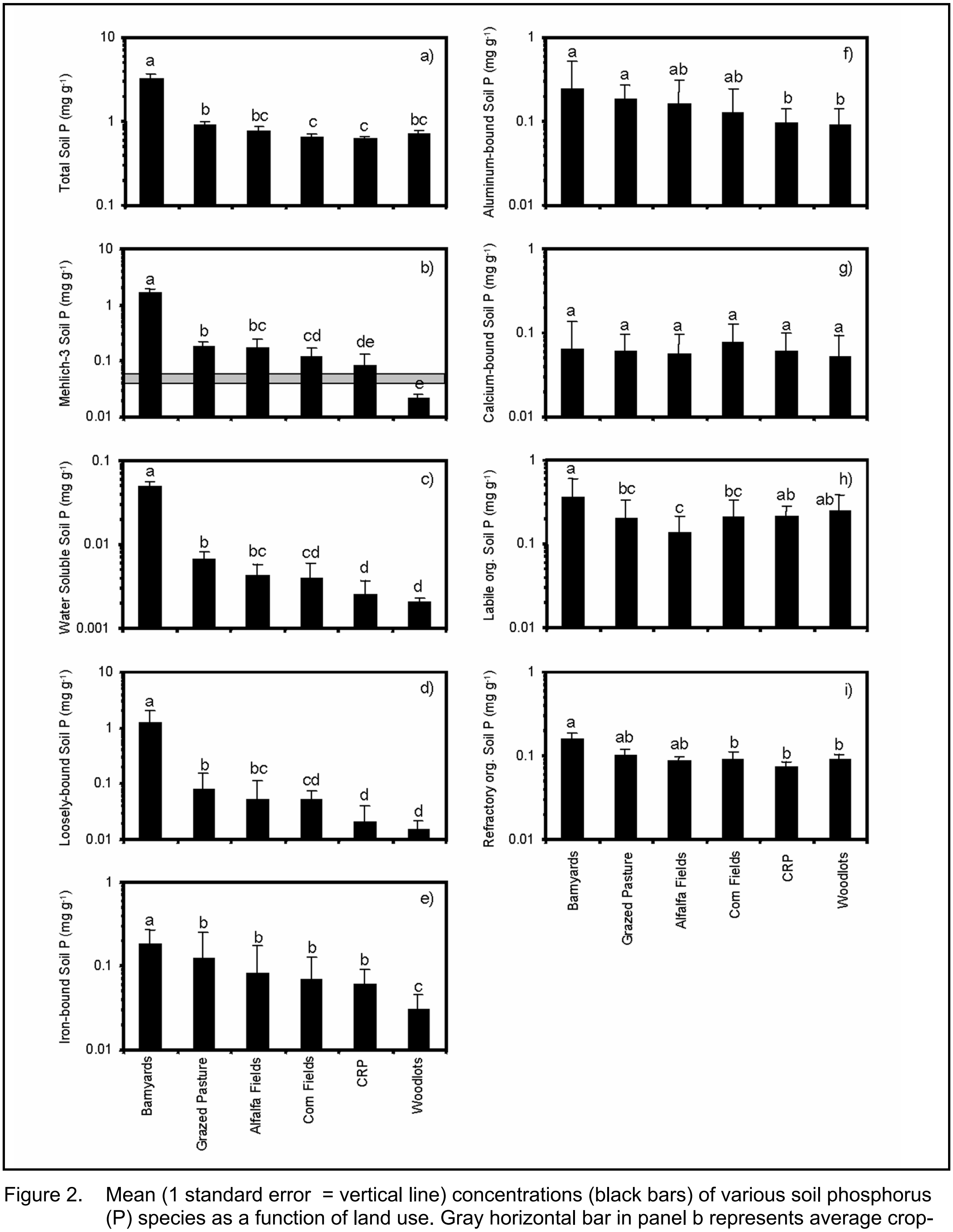

Figure 2. Mean (1 standard error = vertical line) concentrations (black bars) of various soil phosphorus (P) species as a function of land use. Gray horizontal bar in panel b represents average crop-available Mehlich-3 P threshold needs. Different letters above means represent significant differences based on ANOVA (SAS 1994)

recycling pathways in receiving waters. For instance, water-soluble P is directly available for biological uptake. Loosely bound and iron-bound P can become a source for biological uptake via equilibrium reactions between aqueous and particulate phases as suspended particles enter a lake. Once settled to the lake bottom, these forms can be recycled via eH and pH reactions at the sediment-water interface and can contribute to autotrophic productivity. These strong correlation patterns are likely due to amendment of soils with P fertilizers and manure above crop needs. Since both subsidies contain high concentrations of inorganic and water-soluble P, excess additions to soils can result in adsorption onto particles and metal oxides. As P amendments increase over crop needs, binding sites on soils become more saturated with P that can be recycled in receiving waters. In contrast, poor correlations between these same variables and generally lower concentrations for soils in unmanaged land uses such as CRP and woodlots are probably indicative of the lack of P amendment. Thus, runoff of soils from these land uses may have less impact on the P economy of receiving waters.

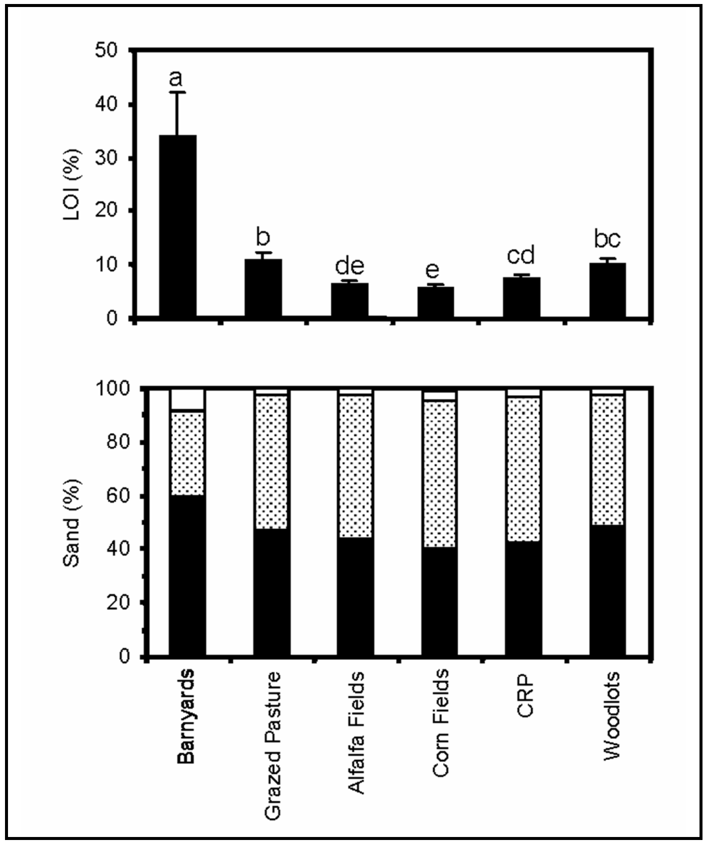

Figure 3. Mean (1 standard error = vertical line) concentrations (black bars) of soil loss-on-ignition (LOI) matter content and the mean percentage of sand, silt, and clay as a function of land-use. Different letters above mean LOI values represent significant differences based on ANOVA (SAS 1994)

Information on biologically labile and refractory components of soils in different land uses, in combination with identification of areas susceptible to runoff, is important in targeting BMP's for reducing P runoff from this and other agricultural watersheds. Eau Galle Reservoir, which receives runoff from the Upper Eau Galle River watershed, is highly eutrophic and exhibits algal blooms in the summer in excess of 100 mg m-3 as chlorophyll. SRP loading (flow-weighted concentration = 0.10 mg L-1) from the watershed during storms contributes directly to high productivity in the lake during the summer (James et al. 2004). In addition, the particulate P component of storm loads is composed of >50 percent loosely bound and iron-bound P, which is reflective of soils from agriculturally managed areas of the watershed. James and Barko (1991, 1993) demonstrated that particulate P loads retained in the lake contribute substantially to the P budget of the lake via diffusive flux as a function of eH and pH and sustain high algal growth in the summer when external P loading is nominal. Thus, it appears that TSS derived from agricultural soils is contributing to high concentrations of biologically labile P forms in P loads entering the reservoir.

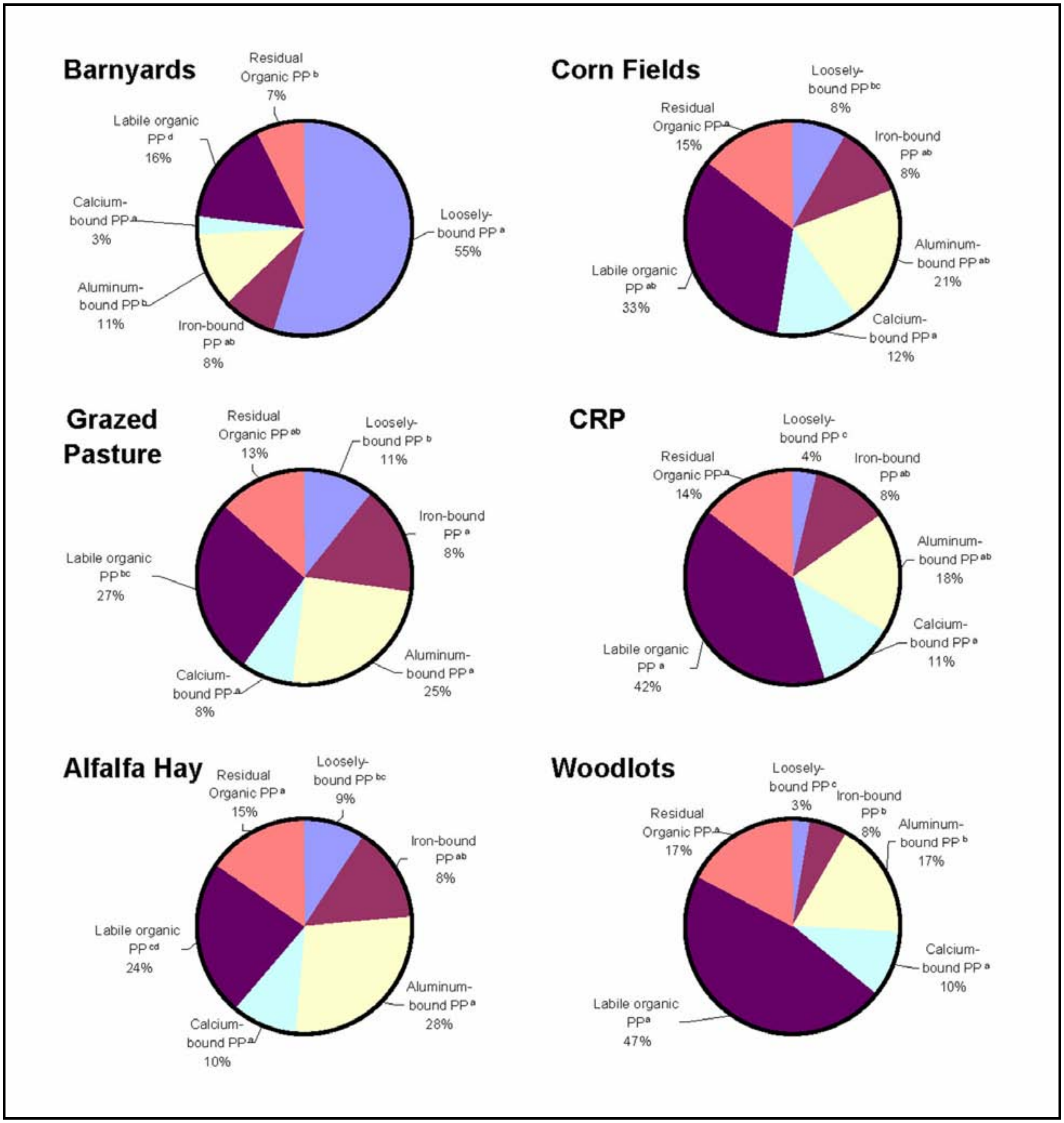

Figure 4. Variations in the percent compositions of various soil phosphorus species as a function of land use. Different letters next to a soil phosphorus variable represent significant differences in relative percent between land uses based on ANOVA (SAS 1994)

Table 3
Correlation Matrices of Various Soil Phosphorus (P) Species for Land Use

Variable (mg g^{-1})	b)	c)	d)	e)	f)	g)	h)	i)
Barnyards (n = 9)								
a) Total P	0.92	0.93	0.91	N.S.	N.S.	N.S.	N.S.	N.S.
b) Mehlich-3 P		0.90	0.98	N.S.	N.S.	N.S.	N.S.	N.S.
c) Water-soluble P			0.87	N.S.	N.S.	N.S.	N.S.	N.S.
d) Loosely bound PP				N.S.	N.S.	N.S.	N.S.	N.S.
e) Iron-bound PP					N.S.	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	N.S.
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								0.76
i) Refractory organic PP								
Forage Pasture (n = 9)								
a) Total P	N.S.	N.S.	0.79	N.S.	N.S.	N.S.	N.S.	N.S.
b) Mehlich-3 P		0.81	0.91	0.72	N.S.	N.S.	N.S.	N.S.
c) Water-soluble P			0.75	N.S.	N.S.	N.S.	N.S.	N.S.
d) Loosely bound PP				0.89	N.S.	N.S.	N.S.	N.S.
e) Iron-bound PP					N.S.	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	N.S.
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								N.S.
i) Refractory organic PP								
Alfalfa Fields (n = 13)								
a) Total P	0.89	0.84	0.86	0.78	0.95	N.S.	N.S.	N.S.
b) Mehlich-3 P		0.98	0.96	0.85	0.93	N.S.	N.S.	N.S.
c) Water-soluble P			0.96	0.75	0.90	N.S.	N.S.	N.S.
d) Loosely bound PP				0.75	0.91	N.S.	N.S.	N.S.
e) Iron-bound PP					0.70	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	N.S.
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								N.S.
i) Refractory organic PP								

(Continued)

Table 3 (Concluded)

Variable (mg g^{-1})	b)	c)	d)	e)	f)	g)	h)	i)
Cornfields (n = 21)								
a) Total P	0.94	0.91	0.94	0.78	0.91	N.S.	N.S.	N.S.
b) Mehlich-3 P		0.99	0.99	0.80	0.91	N.S.	N.S.	N.S.
c) Water-soluble P			0.99	0.76	0.88	N.S.	N.S.	N.S.
d) Loosely bound PP				0.77	0.91	N.S.	N.S.	N.S.
e) Iron-bound PP					0.76	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	N.S.
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								N.S.
i) Refractory organic PP								
CRP (n = 13)								
a) Total P	N.S.	N.S.	N.S.	N.S.	0.76	N.S.	N.S.	N.S.
b) Mehlich-3 P		0.82	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
c) Water-soluble P			N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
d) Loosely bound PP				N.S.	N.S.	N.S.	N.S.	N.S.
e) Iron-bound PP					0.76	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	N.S.
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								N.S.
i) Refractory organic PP								
Woodlots (n = 16)								
a) Total P	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	0.81
b) Mehlich-3 P		N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
c) Water-soluble P			N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
d) Loosely bound PP				N.S.	N.S.	N.S.	N.S.	N.S.
e) Iron-bound PP					N.S.	N.S.	N.S.	N.S.
f) Aluminum-bound PP						N.S.	N.S.	0.63
g) Calcium-bound PP							N.S.	N.S.
h) Labile organic PP								N.S.
i) Refractory organic PP								

SUMMARY: Biologically labile forms of soil P were greatest for agriculturally managed soils, versus CRP and woodlots. Strong correlations existed between total P and Mehlich-3 P, water soluble P, loosely bound P, iron-bound P, and aluminum-bound P for annual and perennial production land uses, suggesting that as P amendments increase over crop needs, binding sites

become increasingly saturated with P that can be recycled in receiving waters. Soils from unmanaged land uses exhibited completely different correlation matrices, suggesting that P speciation might be a useful means of detecting unique soil features as a function of different land-use practices, which can be used in determining relative contributions of source soils to P loads in receiving waters. Predictive capabilities of watershed models may increase by improved discrimination of biologically labile and refractory phosphorus species in source soils of different land-use practices and linkage to transport and transformation processes versus use of total or crop-available soil P.

ACKNOWLEDGMENTS: The authors gratefully acknowledge L. Pommier, ASI Corporation, for performing soil P fractionations and T. Brunner, M. Daniels, K. Johnson, and M. Weiss of the Eau Galle Aquatic Ecology Laboratory, ERDC, for field sampling.

POINTS OF CONTACT: This technical note was written by Messrs. William F. James and Harry L. Eakin of the Eau Galle Aquatic Ecology Laboratory, Environmental Laboratory (EL), Engineer Research and Development Center (ERDC), and Drs. Carlos E. Ruiz and John W. Barko, EL, ERDC. For additional information, contact the manager of the System-wide Modeling, Assessment, and Restoration Technologies (SMART) Program, Dr. Steven L. Ashby (601-634-2387, *Steven.L.Ashby@erdc.usace.army.mil*). This technical note should be cited as follows:

> James, W. F., Eakin, H. L., Ruiz, C. E., and Barko, J. W. (2004). “Soil phosphorus compositional characteristics as a function of land-use practice in the Upper Eau Galle River Watershed, Wisconsin,” *SMART Technical Notes Collection*, ERDC/TN SMART-04-5, U.S. Army Engineer Research and Development Center, Vicksburg, MS.

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